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CALCULATED STRUCTURE, HEATS OF FORMATION AND DECOMPOSITION ENERGETICS OF 1,3-DINITRO,-1,3-DIAZACYCLOBUTANE

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Using HF/6-31G* optimized geometries, the heat of formation of 1,3-dinitro-1,3-diazacyclobutane and the energetics of two possible decomposition reactions were computed by a non-local density functional procedure (deMon). ΔH_f° at 25°C is 351 cal/g; the N–NO_2 dissociation energy is 36.6 kcal/mole, and the activation barrier for symmetrical ring fragmentation is 44.2 kcal/mole.

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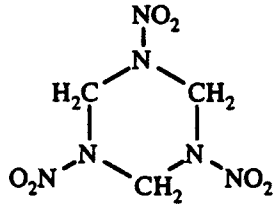
Introduction

1,3,5-trinitro-1,3,5-triazacyclohexane (**1**; RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetraaza-cyclooctane (**2**; HMX) are highly energetic cyclic nitramines.[1,2] Both can be represented by the formula $(CH_2NNO_2)_n$. The smallest member of this series, 1,3-dinitro-1,3-diazacyclobutane (**3**), has, to our knowledge, not yet been synthesized. A possibly significant feature of **3** that is not present in **1** or **2** is strain due to the four-membered ring. This should increase the molecule's energy content, although the effect is likely to be reduced by σ-conjugation of the aza nitrogens' lone pairs.[3]



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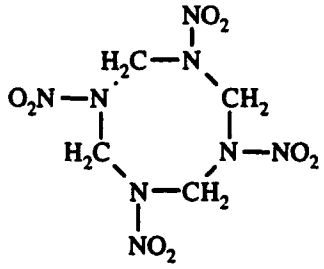

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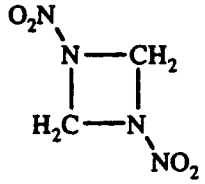

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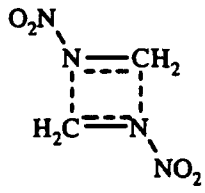

4

A useful measure of energy content is the heat of formation, and one of our present objectives was to compute this for **3**. We also extend earlier preliminary studies of two possible decomposition steps:[4,5] (a) homolytic rupture of an N–NO_2 bond, and (b) dissociation of the ring into two H_2C=N–NO_2 fragments, passing through the transition state **4**.

Methods

HF/6-31G* optimized geometries and vibration frequencies were computed for **3** - **7** with the GAUSSIAN 92 program;[6] the frequencies were scaled by 1/1.12.[6,7] (For **5** and **6**, the unrestricted Hartree-Fock approach was used.) Single point runs were then carried out for each structure with the non-local density functional (DF) code deMon,[8] using the Gaussian DZVPP basis set; the exchange-correlation energies were calculated by means of the generalized gradient approximation (GGA).[9,10] These DF results were used in computing the reaction energetics.

Standard gaseous heats of formation were obtained by computing ΔE (DF) for the formation of each molecule from its elements, combining this with translational, rotational and vibrational contributions and converting the result to ΔH° at 25°C using the ideal gas approximation.[11,12] Empirical bond and group correction terms were also included.[11,12]

Results

The HF/6-31G* optimized geometries of **3** - **7** are given in Table I. Although experimental values are known only for NO_2 (**6**), data relevant to **3** and **5** are in crystallographic[13,14] and electron diffraction[15] studies of RDX (**1**) and 1,3,3-trinitroazetidine, and an MCSCF structure is available for **7**.[16] In general, there is good agreement, although the HF/6-31G* procedure tends to

underestimate N–O bond lengths by roughly 0.03 Å. Our structures for **3** and **5** - **7** do correspond to local energy minima (no imaginary frequencies) and **4** is a transition state (one imaginary frequency). The HF/6-31G* and the DF-GGA/DZVPP energies of **3** - **7** are in Table II.

The strain energy of **3** was estimated by the isodesmic reaction procedure,[7] which involves writing a hypothetical chemical process in which the number of bonds of each type remains the same but their mutual relationships have changed. ΔE for such a reaction is interpreted as revealing any deviations from bond energy additivity, due to strain, resonance stabilization, etc.

At the HF/6-31G* level, taking $H_2N–NO_2$ and H_3C-NH_2 to be the reference molecules and using energies obtained in this work and from archives,[17] we find the strain energy of **3** to be 8.6 kcal/mole. This is in good agreement with our earlier HF/3-21G value of 9.5 kcal/mole.[3] As a test, we also computed the HF/6-31G* strain energy for cyclopropane, using an analogous isodesmic reaction, and obtained 26.3 kcal/mole, which is close to the quoted value of 28.3 kcal/mole.[18]

Our estimated standard gaseous heat of formation at 25° C for **3** is +52.0 kcal/mole. We believe this to be reliable, since the very similar RDX (**1**) was part of our data base in determining the correction terms, and our procedure reproduces its measured ΔH_f° [19] to within 0.1 kcal/mole.[12] Our ΔH_f° for **3** exceeds that of RDX by 6.2 kcal/mole; this may reflect the strain in **3**.

Using the data in Table II, with zero-point energies taken into account, the DF $N–NO_2$ dissociation energy is 36.6 kcal/mole. The overall ΔE for the ring fragmentation is 17.0 kcal/mole, but the activation barrier for this process is 44.2 kcal/mole. $N–NO_2$ dissociation and ring fragmentation are therefore roughly similar in terms of their energetic requirements.

Discussion

The heat of formation, expressed on a mass basis, is a key determinant of the detonation and propellant properties of an energetic material.[20] Thus it is noteworthy that our value for **3**, 351 cal/g, is 70% larger than that of RDX (**1**), 206 cal/g.

The $N–NO_2$ dissociation energy, 36.6 kcal/mole, is somewhat less than the 40-50 kcal/mole range typical of $N–NO_2$ bonds,[21-24] possibly reflecting some release of strain upon breaking the bond. In view of evidence that rupture of the $N–NO_2$ bond is an important factor in nitramine decomposition,[21,25-27] the weakness of these bonds in **3** suggests that it might possess a rather high sensitivity to shock and/or impact. A similar conclusion is reached on the basis of a correlation relating nitramine shock sensitivity to the $N–NO_2$ bond lengths and the molecular weight; [28] **3** is predicted to have a shock sensitivity very close to those of RDX (**1**) and HMX (**2**). Nevertheless, its relatively high energy content, as reflected in its heat of formation, should stimulate continued synthetic efforts.

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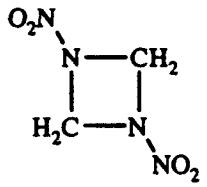
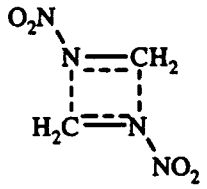
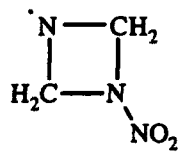
Table I. HF/6-31G* optimized geometries.

Molecule		Distances (Å)		Angles (deg)	
	**3**	C–N:	1.466	N–C–N:	87.3
		N–N:	1.355	C–N–C:	92.7
		N–O:	1.191	C–N–N:	119.9
				N–N–O:	116.4
				O–N–O:	127.2
				N–C–N–N:	127.1
				C–N–N–O:	34.6, 147.7
	**4**	C–N:	1.343	N–C–N:	92.0
		C···N:	1.991	C–N–C:	88.0
		N–N:	1.369	C–N–N:[b]	114.1
		$N–O_a$:	1.191	$N–N–O_a$:[b]	115.0
		$N–O_b$:	1.197	$N–N–O_b$:[b]	119.4
				O–N–O:	125.6
				N–C–N–C:	0.0
				$C–N–N–O_a$:[b]	156.7
				$C–N–N–O_b$:[b]	24.2
	**5**	$C–N(NO_2)$:	1.466	N–C–N:	90.3
		C–N:	1.459	$C–N(NO_2)–C$:	88.8
		N–N:	1.349	C–N–C:	89.3
		N–O:	1.193	C–N–N:	121.2
				N–N–O:	116.6
				O–N–O:	126.8
				C–N–C–N:	8.5
				N–N–C–N:	134.9
				C–N–N–O:	35.9, 145.8
$\cdot NO_2$	**6**	N–O:	1.165 (1.197)[a]	O–N–O:	136.1 (133.8)[a]
	7	C–N:	1.254	C–N–N:	113.7
		N–N:	1.417	O–N–O:	126.6
		$N–O_a$:	1.180	$N–N–O_a$:	113.9
		$N–O_b$:	1.193	$N–N–O_b$:	119.5
				$C–N–N–O_a$:	157.1
				$C–N–N–O_b$:	24.1

[a]Experimental values for NO_2, in parentheses, from Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data*, **1979**, *8*, 619.

[b]These angles are within each $H_2C=N–NO_2$ portion.

Table II. Calculated energies.

Molecule	Total Energy[a]		Zero-point energy
	HF/6-31G*	DF-GGA/DZVPP//HF/6-31G*	(HF/6-31G*),
		(hartrees)	(kcal/mole)
3	-594.97670	-599.02944	58.13
4	-594.86945	-598.95329	54.53
5	-390.91306	-393.62772	47.53
6	-204.03149	-205.33525	5.52
7	-297.47560	-299.49753	26.76

[a]This corresponds to energy minimum at 0°K.